4-chloro-2-methylphenoxyacetic acid concentration and additional carbon source determine the measured centimetre-scale vertical variability of mineralization potential around the groundwater table

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4-chloro-2-methylphenoxyacetic acid concentration and additional carbon source determine the measured centimetre-scale vertical variability of mineralization potential around the groundwater table

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Introduction

The phenoxyacid herbicide, MCPA (4-chloro-2-methylphenoxy-acetic acid) related to the plant growth hormone is one of the most commonly used herbicides for controling broadleaf weeds.

MCPA leaching from agricultural soil threatens groundwater which is a main drinking water resource in many countries.

Soil and groundwater systems are complex with a high degree of spatial variability in terms of physical, chemical and biological properties.

In our previous work, centimetre-scale vertical variability in mineralization potential of 2,4-D and MCPA at 1 mg kg^{-1} was found and linked to uneven distribution of *tfdA* genes involved in MCPA degradation in the oligotrophic saturated zone (Batıoğlu-Pazarbaşı *et al.*, 2012).

In our current study, MCPA was chosen as a model compound due to its more even distribution of mineralization potential than that of 2,4-D. The effects of MCPA concentration and additional carbon sources on the centimetre-scale vertical variability of mineralization potentials were studied in the oligotrophic interface of unsaturated-saturated zones.

Hypothesis

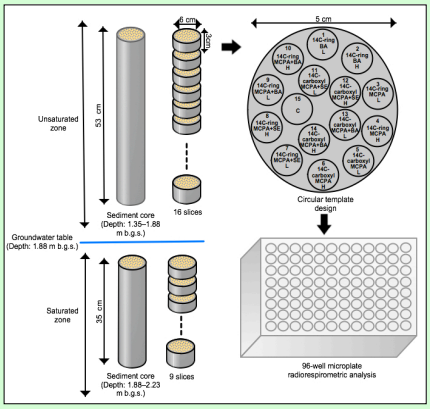
In non-contaminated or slightly contaminated groundwater systems, microorganisms are more adapted to oligotrophic conditions due to lack of light and low amount of available energy.

We therefore hypothesize that MCPA mineralization potential at field-relevant concentration (~10 µg kg^{-1}) is more evenly distributed at centimetre scale when compared to higher concentration (10 mg kg^{-1}), where tolerant populations might be more unevenly distributed.

We also hypothesize that addition of external carbon sources, mimicking an inflow of assimilable substrates, might enhance MCPA mineralization in the unsaturated and saturated zones due to the stimulated activity of populations co-metabolically degrading MCPA.

Methods

Overview of centimetre-scale sampling approach



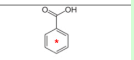
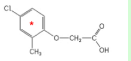
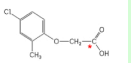
SE: Soil Extract, BA: Benzoic acid, L: Low (field-relevant) concentration, H: High concentration, m b.g.s.: meter below ground surface

Sediment was sampled both above (unsaturated zone) and below (saturated zone) the water table of a groundwater aquifer located near Fladerne Creek area, Jutland, Denmark. The area has been used as farmland since 1920 and exposed only to MCPA and no other phenoxy acid herbicides.

The first and second cores were divided into 16 and 9 slices with 3 cm intervals; and top and bottom slices were discarded to prevent contamination.

A circular template with sampling holes was positioned on the surface of each slice and a 0.4 g sediment sample was collected from each hole using a 2-mL tip-cut syringe. The sediment samples were transferred to 96-well microplates and used for quantification of mineralization potential.

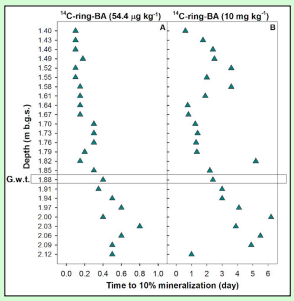
Experimental design and the molecular structures of model compounds

Microtiter plate number	^{14}C-compound	Molecular Structure
1	^{14}C-ring-BA	
2,4,5	^{14}C-ring-MCPA ^{14}C-ring-MCPA + SE ^{14}C-ring-MCPA + BA	
3,6,7	^{14}C-carboxyl-MCPA ^{14}C-carboxyl-MCPA + SE ^{14}C-carboxyl-MCPA + BA	

The mineralization was followed both at low and high concentrations for each experimental set up.

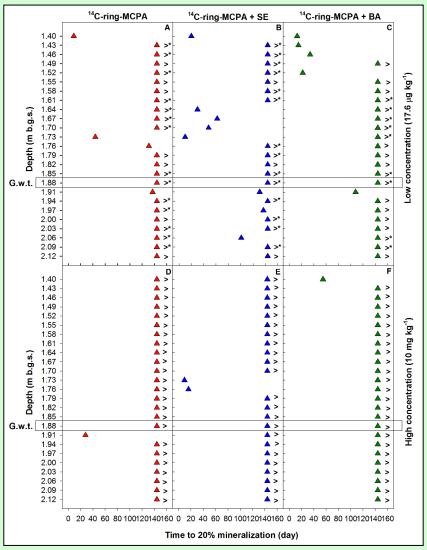
Results

Centimetre-scale vertical variability in mineralization potentials of benzoic acid at field-relevant and higher concentrations



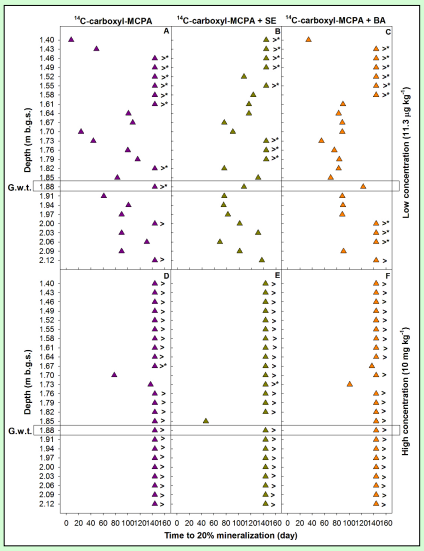
Unsaturated zone (1.40–1.88 m b.g.s.), G.w.t. (Groundwater table) (1.88 m b.g.s.) and saturated zone (1.88–2.12 m b.g.s.)

Centimetre-scale vertical variability in mineralization potentials of ^{14}C-ring-MCPA at field-relevant and higher concentrations



> indicates that the duration exceeds 144 days
* indicates 5%–10% mineralization activity

Centimetre-scale vertical variability in mineralization potentials of ^{14}C-carboxyl-MCPA at field-relevant and higher concentrations



> indicates that the duration exceeds 144 days
* indicates 5%–10% mineralization activity

Conclusions

The mineralization potential of benzoic acid indicating general bacterial activity at field-relevant concentration was more evenly distributed than that at higher concentration, but benzoic acid was mineralized at all depths for both concentrations indicating that there was no bacterially inactive zones along the unsaturated and saturated zones.

The mineralization potential of MCPA at field-relevant concentration was also more evenly distributed than that at higher concentration, indicating the presence of bacteria adapted to degrade MCPA at low concentration.

The degradation of ^{14}C-carboxyl-MCPA was more widespread than that of ^{14}C-ring-MCPA, indicating that the degradation potential towards the side chain of MCPA was more frequently encountered than the capacity to degrade the ring structure.

Attempts to stimulate cometabolic MCPA degradation by addition of soil extract or benzoic acid as substrates were tested. A decrease in the degradation of the side chain, and an increase in the degradation of the MCPA ring structure were evident, which might be explained by the activity of non-specific di-oxygenases expressed during growth on soil extract or benzoic acid acting on the aromatic ring of MCPA.

In conclusion, groundwater bacteria can adapt to herbicide degradation at field-relevant concentrations, and that mineralization potential in some cases can be stimulated by inflow of additional fresh substrates.

Acknowledgements

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Reference

Batıoğlu-Pazarbaşı M, Bælum J, Johnsen AR, Sørensen SR, Albrechtsen H-J & Aamand, J (2012) Centimeter-scale vertical variability of phenoxy acid herbicide mineralization potential in aquifer sediment relates to the abundance of *tfdA* genes. *FEMS Microbiol Ecol* **80:** 331–341.